

Nonextensive Reaction Rate

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The Kramers' survival probability has been generalized by using nonextensive formalism. This nonextensive survival probability is studied in detail and associated Kramers' rate has been calculated in the high and low viscosity limit. It has been showed that the proportionality of nonextensive Kramers' rate to the nonextensive friction term in the high viscosity limit changes to inverse proportionality in the low viscosity limit. It has also been observed that friction constant of nonextensive processes is of rescaled form of the ordinary frictional term. Since the relation between the ordinary rate and nonextensive rate is found out to be linear, the Arrhenius nature of the Kramers' rate is preserved. By using experimental results related to CO rebinding to myoglobin after photodissociation, we conclude that nonextensivity plays an important role in protein reactions.

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I. INTRODUCTION

A nonextensive generalization of the standard Boltzmann-Gibbs (BG) entropy has been proposed by C. Tsallis in 1988 [1-4]. This new definition of entropy is written in terms of a parameter q , a positive constant k which becomes usual Boltzmann constant in the limit as q approaches 1, and probabilities of microstates. This form of entropy breaks the additivity of ordinary definition of entropy since for two independent systems, there is an additional term which consists of multiplication of these two distinct terms of entropy together with the parameter $(q-1)$. Therefore, the entropic index q is a real number which characterizes the degree of nonextensivity. When it attains the value 1 as a limiting case, nonextensive formalism reduces to ordinary Boltzmann formalism which means that BG statistics is a special case of nonextensive statistics. Nonextensive formalism is used in systems with long-ranged interactions, long-ranged memories and systems which evolves in fractal-like space-time. Even though BG statistics can be used successfully in investigating extensive systems, physical systems such as Euler two-dimensional turbulence [5], high energy collisions [6-9], nematic liquid crystals [10] and stellar polytropes [11] as well as nonisotropic rigid rotator model [12], Fokker-Planck systems [13,14] can be given as examples for which nonextensive formalism has been used successfully.

After this brief survey of nonextensive formalism, we turn our attention to reaction rate problem in the form formulated by Kramers [15]. He was able to calculate the dependence of escape probability on viscosity and temperature through his model. Kramers' model has been extended by scientists like Hänggi et al. [16], Montroll and Schuler [17] for example to consider non-Markovian effects [18]. It is worth to notice that all these attempts ended up in having a survival probability which decays exponentially in time. The need of generalizing Kramers' rate in such a way as to have a nonexponential decay in time is due to the off-equilibrium condition since this condition creates genuine power laws as noted by Refs. [19, 20, 21]. Indeed, it has been shown in Ref. [14] that nonlinear Fokker-Planck equations can result in survival probabilities of the q -exponential form. Moreover, Plastino et al. [22] considered nonlinear reaction-diffusion equations with nonlinear diffusion and reaction term and showed that they possess exact time-dependent particular solutions of Tsallis' maximum entropy form. Recently, Niven [23] approached the reaction rate problem in nonextensive formalism from a different point of view by considering q as the reaction order. In the next Section, by generalizing survival probability using nonextensive formalism, we obtain a survival probability which is of the form of an inverse power law in the asymptotic regime. We also compare this to some recent experimental findings in protein rebinding [24, 25, 26]. In Ref. [27], an attempt has been made to generalize the reaction rate of Kramers through the use of Mittag-Leffler function where survival probabilities have been in the form of inverse power law asymptotically. In this study, we generalize the Kramers' rate using q -exponentials and obtain survival probabilities of inverse power

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law. Tsallis et al. in Ref. [28, 29] uses the same set of data in order to explain fractal behavior of the experiment through Lyapunov exponents. Our approach is based on Kramers' model and off-equilibrium conditions which generate genuine inverse power laws. Within this approach, not only experimental findings in protein rebinding [24, 25, 26] will be explained but also the inverse power law behavior found in Ref. [21] in which a stretched exponential and inverse power law distribution with different powers are interpolated. The Mittag-Leffler function requires the same power for stretched exponential and inverse power law behavior, therefore cannot explain the situation in Ref. [21] whereas the survival probability of the form of q -exponential can.

II. NONEXTENSIVE REACTION RATES

Kramers [15] considered a point particle in phase space which is initially trapped in an asymmetric well under a potential V . In addition to this, the particle is also assumed to be subject to the random Brownian forces of the surrounding medium in thermal equilibrium. The particle can escape over the potential barrier which means a transition from the well of reactants to the well of products. Kramers also assumed that the height of the potential barrier is very large compared with the temperature of the environment ensuring a slow diffusion process from the well of reactants to the well of products. It is also assumed that the potential associated with the well of reactants is given by

$$V(x_{\min}) = \frac{1}{2}m(2\pi\omega^2)x^2, \quad (1)$$

whereas the potential around the barrier is given by

$$V(x_{\max}) = \Delta V - \frac{1}{2}m(2\pi\omega'^2)(x - x_{\max})^2, \quad (2)$$

The parameters x_{\min} and x_{\max} are the coordinates whereas ω and ω' are the corresponding angular frequencies for the well of reactants and products respectively. $\Delta V = V(x_{\max}) - V(x_{\min})$ is the height of the potential barrier and m denotes the mass of the particle. The ordinary (i.e., extensive) survival probability is then given in terms of usual exponential function as

$$p(t) = \exp(-rt), \quad (3)$$

where r denotes the rate of the process and t is time parameter.

Kramers particularly studied reaction rates for overdamped and underdamped cases. For the former, he found [15, 30]

$$r \cong \frac{1}{2\pi m}\eta^{-1}\sqrt{V''(x_{\min})|V''(x_{\max})|}e^{-\beta\Delta V}, \quad (4)$$

and

$$r \cong \eta\beta\Delta V e^{-\beta\Delta V}, \quad (5)$$

for the latter, where β is $(k_B T)^{-1}$ and η is the Brownian friction constant [15]. The double prime indicates the second derivative with respect to position x . The overdamped case which is also called the case of large viscosity in Kramers' paper refers to the case when the effect of the Brownian forces on the velocity of the particle is much larger than that of the external force associated with the potential of the well. The underdamped case makes the assumption that no Brownian forces are present so that the particle will simply oscillate. This case is also referred to as the case of low viscosity in Kramers' paper [15]. A brief explanation for the reaction rate expressions used in this paper for overdamped and underdamped cases is given in the Appendix. From Eqs. (4) and (5), it is trivial to observe that $r^{-1} \propto e^{E/T}$ where $E \equiv \Delta V/k_B$ i.e., inverse of the Kramers' rate, both in the high and low viscosity cases, conforms to Arrhenius activation formula.

Before proceeding with nonextensive formalism, we must inspect Eq. (3) and observe that ordinary reaction rate can be calculated as following:

$$r \equiv \frac{p(t=0)}{\widehat{p}(u=0)}, \quad (6)$$

where $\widehat{p}(u)$ is the Laplace transform of the function $p(t)$ given by Eq. (3). Laplace transform $\widehat{p}(u)$ of $p(t)$ is defined by $\widehat{p}(u) = \int_0^\infty p(t)e^{-ut}dt$. Note that when the Laplace variable u is equal to zero, we have the normalization of the function $p(t)$.

From a mathematical point of view, nonextensive formalism is being formulated by using the q -deformed logarithm and q -deformed exponential which can be given as

$$\ln_q x \equiv \frac{x^{1-q} - 1}{1 - q} \quad \exp_q x \equiv [1 + (1 - q)x]^{1/(1-q)}. \quad (7)$$

As expected, these functions become the usual logarithmic function and exponential function respectively as $q \rightarrow 1$. Now, we begin by writing ordinary exponential in Eq. (3) as a q -exponential i.e., we write [14]

$$p_q(t) = \exp_q(-rt) = [1 + (q - 1)rt]^{1/(1-q)}. \quad (8)$$

$p_q(t)$ is normalized as a survival probability in the sense that it is equal to 1 at $t=0$, mimicking the exponential case given by Eq. (3). Then, we rewrite Eq. (6) in the form

$$r_q \equiv \frac{p_q(t=0)}{\widehat{p}_q(u=0)}. \quad (9)$$

where the Laplace transform is defined in the same way above. The Laplace transform $\widehat{p}_q(u)$ at $u = 0$ is the integral of the function $p_q(t)$ from zero to infinity i.e., its normalization. This is obtained as

$$\widehat{p}_q(u=0) = \frac{1}{r} \frac{1}{2 - q}, \quad q < 2, \quad (10)$$

where r is the ordinary rate of the process i.e., $r = r_{q \rightarrow 1}$. The constraint $q < 2$ has been put since the Laplace integral in the denominator of Eq. (9) otherwise diverges. Since $p_q(t=0) = 1$, we obtain the generalized reaction rate as

$$r_q = (2 - q)r_{q \rightarrow 1}, \quad q < 2. \quad (11)$$

The Eq. (9) is valid for both overdamped and underdamped cases as long as $r_{q \rightarrow 1}$ is taken to be of the form in Eqs. (4) and (5) i.e., the extensive reaction rates for the overdamped and underdamped cases. For the former case, we get

$$r_q = \eta_q^{-1} \frac{\sqrt{V''(x_{\min})/V''(x_{\max})}}{2\pi m} e^{-\beta\Delta V}, \quad (12)$$

where

$$\eta_q = \frac{\eta}{(2 - q)}. \quad (13)$$

For the latter, we have

$$r_q = \eta'_q \beta \Delta V e^{-\beta\Delta V}, \quad (14)$$

where

$$\eta'_q = (2 - q)\eta. \quad (15)$$

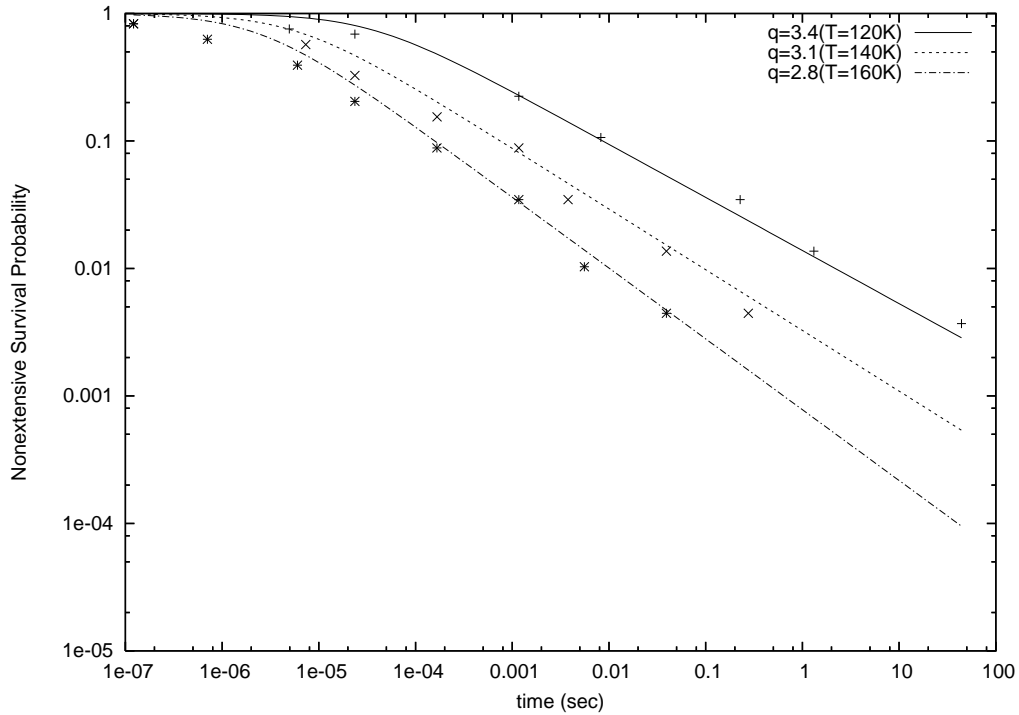


FIG. 1: The nonextensive survival probability $p_q(t)$ given by Eq. (8) versus time for the temperatures 120 K, 140 K and 160 K corresponding to the values of q equal to 3.4, 3.1 and 2.8 respectively.

From Eqs. (13) and (15), we see that $\eta/\eta_q = (2 - q)$ and $\eta'_q/\eta = (2 - q)$: The nonextensive friction constants (i.e., η_q and η'_q in the overdamped and underdamped cases respectively) is rescaled by the same factor $(2 - q)$, we also note that nonextensive formalism gives rise to turnover in the dependence of friction since $r_q \propto \eta_q^{-1}$ and $r_q \propto \eta'_q$ in the overdamped and underdamped cases respectively as can be seen from Eqs. (12) and (14). This turnover is already inherent in the Eqs. (4) and (5) which is the extensive theory and we successfully preserved this form in nonextensive formalism.

The Kramers' theory is also being used for investigating the chemical reactions in the proteins. However, the related survival probability in this case is non-exponential. In fact, the experiment of ligand CO rebinding to myoglobin after photodissociation as investigated by Iben et al. [24] shows an inverse power law behaviour in the time asymptotic limit until one reaches a certain higher critical temperature T_c . Glöckle and Nonnenmacher [25] assumed this power to be temperature dependent and equal to $\alpha(T) = 0.41T/120$ to take the change in the protein-solvent system into account. In Fig. 1, we provide some plots for survival probability $p_q(t)$ for $q = 2.8, 3.1$ and 3.4 which correspond to these experimental findings [26, 27] for temperature values $T = 160$ K, 140 K and 120 K respectively. This plot shows that as temperature increases, the nonextensivity of the system becomes less and less dominant.

III. RESULTS AND DISCUSSIONS

We have studied nonextensive generalization of Kramers' reaction rate by writing the survival probability as a q -exponential. We showed that the dependence of nonextensive Kramers' rate to the nonextensive friction term in the high viscosity limit changes to inverse proportionality in the low viscosity limit. In fact, this is a property of the ordinary Kramers' theory and nonextensive formalism preserves this important turnover. We calculated nonextensive reaction rate by making use of Laplace transform and observed that the relation between the extensive and nonextensive cases is found out to be linear. Therefore, the Arrhenius nature of the Kramers' rate is preserved. We then

referred to some experimental data concerning the ligand CO rebinding to myoglobin after photodissociation. In this experiment, survival probability is of the form of inverse power law with a power depending on temperature due to change in the protein-solvent system in the time asymptotic limit. It has been shown in Fig.1 by plotting nonextensive survival probability for various temperature values that some q values which are different than 1 correspond to these distinct cases. We propose this to be a signature of nonextensivity in the photodissociation of the process of CO rebinding to myoglobin. Moreover, Fig.1 shows that as temperature increases, the nonextensivity of the system becomes less and less dominant. Therefore, this phenomenological picture is in accordance with the experimental findings which indicate that the survival probability becomes exponential at a higher temperature. This transition from power law to exponential can be seen by the inspection of Fig.1, since as temperature continues to increase, we expect the nonextensivity parameter q to drop to 1 at some higher critical temperature, which means the transition to exponential case. In Ref [27], this behavior has been tried to be explained by the use of Mittag-Leffler function, but we believe that nonextensive scenario gives a more adequate picture since Mittag-Leffler forces one to interpolate between the stretched exponential and inverse power law behavior with same exponent only. In fact, if one inspects Ref. [21], one immediately sees that it is a stretched exponential and inverse power law distribution with different powers to be interpolated. This cannot be done using Mittag-Leffler function, which requires the same power for stretched exponential and inverse power law behavior. Our final remark is about Ref. [28, 29], which uses the same experimental findings as we did in Fig.1, but the novelty of this paper compared to Ref. [28, 29] lies in the use of different approaches. We tried to generalize Kramers' rate in a way which will provide survival probabilities of inverse power law whereas Ref. [28] treats the same subject from the point of view that the same set of data can be used in order to explain fractal behavior of the experiment through Lyapunov exponents.

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APPENDIX A

The reaction rate for the underdamped case is given by Eq. (5) in our paper and this equation is exactly the same expression in Kramers' original paper i.e., Eq. (28) in Ref. [15]. The reaction rate for overdamped case i.e., Eq. (4) in this paper is not found in Kramers' article [15] but is due to Risken [30]. Kramers' rate for overdamped case is given by Eq. (17) in Ref. [15] in the following form

$$r \cong \frac{2\pi\omega\omega'}{\eta} e^{-\beta\Delta V}. \quad (\text{A1})$$

In order to see the equality of the equation above and ours given by Eq. (4), we take derivative of Eqs. (1) and (2) with respect to position two times and obtain

$$V''(x_{\max}) = -m(2\pi\omega)^2 \quad (\text{A2})$$

and

$$V''(x_{\min}) = m(2\pi\omega)^2. \quad (\text{A3})$$

Substitution of Eqs. (A2) and (A3) into Eq. (4), we see that Eq. (A1) follows. Note that we also need to take mass term equal to unity as Kramers did. Therefore, Eq. (17) in Kramers' paper and our equation (4) due to Risken is the same.

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